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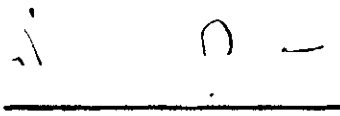

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A STUDY OF

TIN (IV) - BROMIDE COMPLEXES IN SOLUTION

A THESIS

Presented to

the Faculty of the Graduate Division

by

Vernon Ray Porter

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

Georgia Institute of Technology

September, 1960

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A STUDY OF

TIN (IV) - BROMIDE COMPLEXES IN SOLUTION

Approved:

[signature]

Date Approved by Chairman: 13 September 1960

ACKNOWLEDGMENTS

I wish to thank the Atomic Energy Commission for the financial support of this research and the Georgia Institute of Technology for several grants-in-aid and an assistantship. But particularly, I want to thank Dr. H. M. Neumann for the suggestion of the problem and for his unfailing encouragement and invaluable suggestions.

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SUMMARY

The purpose of this investigation is to identify the species of Sn(IV)-Br complexes that exist in solution and to find the conditions most favorable for their existence. This study is to be done chiefly by spectrophotometry.

The following description outlines in a general way the attack on the problem. First, by isolating specific compounds and determining their spectra, some certainty is attached to the identification of species in solution. Second, by varying the conditions in aqueous solutions, the particular set of conditions can be found at which the characterized species are predominant. Third, by studying the spectral changes accompanying changes in hydrogen ion and bromide ion concentrations, some conclusions can be drawn about additional species.

In accordance with the above scheme, stannic bromide was prepared and purified. Solutions in three non-polar non-aqueous solvents each had a spectrum with a maximum at 240 mμ with a shoulder at 272 mμ. This spectrum is characteristic of discrete $SnBr_4$ molecules. The spectra of stannic bromide were also measured in ethyl ether, acetonitrile, and chloroform. From the spectra (a maximum about 250 mμ) and other data, the $SnBr_4 \cdot 2Solvent$ species was shown to be present. The spectra of stannic bromide in several concentrations of hydrobromic acid were also qualitatively measured and were found to possess two large maxima about 280 mμ and 305 mμ, which degenerated with decreasing HBr concentration.

The stannic bromide was used to prepare three hexabromostannate salts. They were shown, by analysis, to have a Br/Sn ratio of six. The same spectrum, with a double maximum at 280 mμ and 305 mμ, was produced by each salt when dissolved in 8.7 M HBr, which showed that the anion was responsible for the spectra. Spectra were also measured in carefully controlled HBr-LiBr solutions, and the changes in the spectra with varying hydrogen ion and bromide ion concentrations were noted. They were interpreted to mean that the hexabromostannate ion, maxima at 280 mμ and 305 mμ, is the primary species when the bromide concentration is above eight molar, and the hydrogen concentration is above one molar. Below these concentrations an $SnBr_4(OH)_y(H_2O)_z^{-y}$, such that y plus z equals two, appears to form. An $SnBr_5(OH)_y(H_2O)_z^{-y-1}$ ion, such that y plus z equals one, seems to be a minor species with a maximum near 270 mμ. This peak is also found when hexabromostannates are dissolved in acetonitrile. The addition of bromide ion to the acetonitrile solutions produces a double peak characteristic of the hexabromostannate ion.

An investigation was also made of the species extracted into isopropyl ether from Sn(IV)-HBr solutions. Species with a Br/Sn ratio of five were indicated.

The solid state spectrum of $SnBr_6^{=}$ was also measured by use of the KBr pressed disk technique. Absorption maxima at 335 mμ and 290 mμ were found.

CHAPTER I

INTRODUCTION

Discussion.--The primary purpose of this study is to investigate the species of Sn(IV)-Bromide complexes that exist in aqueous solutions containing various concentrations of bromide, Br^-, ions. A secondary investigation is made of stannic bromide, $SnBr_4$, because of its fundamental relationship to the Sn(IV)-Br complexes.

It was expected that in aqueous solution a variety of species would be present, and that these species would fit the general formula $SnBr_x(OH)_y(H_2O)_z^{z-2}$, where the sum of x, y, and z is six.

The following description outlines in a general way the attack on the problem. First, by isolating specific compounds and determining their spectra, some certainty is attached to the identification of species in solution. In particular, this technique seemed suited to the $SnBr_6^=$ ion, and also, to a lesser extent, $SnBr_4(H_2O)_2$. Second, by varying the conditions in aqueous solutions, the particular set of conditions can be found at which the characterized species are predominant. Third, by studying the spectral changes accompanying changes in hydrogen ion and bromide ion concentrations, some conclusions can be drawn.

The existence of six-coordinated Sn(IV) is now generally accepted. In particular the stannate ion, $Sn(OH)_6^=$, and the hexahalostannate ions, $SnX_6^=$ (X = Cl, Br, I), are recognized as distinct units. Most of the evidence supporting this idea has been derived from studies

in the solid state. Wycoff (1) has shown the octahedral nature of the stannate ion. Corrozzi (2) proved the isomorphic properties of $SnX_6^=$ ions (X = Cl, Br) with $SeX_6^=$, $PtX_6^=$, and $PbX_6^=$ ions, in salts of the type M_2SnX_6. X-ray diffraction techniques employed by Dickenson (3) showed that in $(NH_4)_2SnCl_6$ and in K_2SnCl_6 the M^+ ions and the $SnCl_6^=$ ions form a face centered cubic unit cell. Both Markstein (4) and Ketelaar (5) examine in detail the structures of the NH_4^+, K^+, Rb^+, and Cs^+ hexabromostannates, M_2SnBr_6.

The primary evidence for octahedral $SnX_6^=$ ions in solution comes from Raman spectral studies. In studying the hydrolysis of $SnCl_4$, Gueron (6) found evidence for the octahedral $SnCl_6^=$ in aqueous solutions. One of the most recent and most convincing argument for the existence of $SnBr_6^=$ in solution is the Raman work of Woodward and Anderson (7). They report the existence of the octahedral $SnBr_6^=$ as the only species when the total bromide concentration is above eleven molar in hydrobromic acid. However, the Sn(IV) concentration is one molar. Thus, the HBr concentration is really only about five molar. Therefore, the small concentration of water, as compared to those used in this investigation, may create a more favorable condition for the formation of the hexabromostannate ion. Their data on Sn(IV) in HCl solutions seems to support this idea, as they get evidence for only $SnCl_6^=$ at HCl concentrations where UV spectra (very dilute in Sn(IV)) indicate that some hydrolysis has occurred.

Lingane (8), using polarography, found that Sn(IV) in perchloric acid, presumably the hexaqua species, did not give satisfactory waves. However, when ammonium chloride or ammonium bromide and the correspond-

ing hydrohalic acid were present in solution and polarographic waves were fully developed. This indicates that Sn(IV)-halo species were generated by the added halide and hydrogen ions.

In this study the concentrations of the solutions rarely are as large as 0.01 M in Sn(IV). Therefore, hydrolysis of the $SnBr_6^{=}$ ion is a major point of interest. The type of hydrolysis involved is a stepwise attack by water upon the hexabromostannate ion resulting in the following equilibrium:

$$SnBr_6^{=} + nH_2O \rightleftharpoons (SnBr_{6-n}(OH)_n)^{=} + nHBr.$$

Thus, high HBr concentrations should favor the formation of the more brominated species, n = 0, 1, or 2. The work of Spacu and Dick (9) seems to indicate that they had isolated salts of the $SnBr_5OH^{=}$ ion and the $(SnBr_4(OH)_2)^{=}$ ion, however, these compounds were isolated from organic solutions and may not represent the predominant aqueous species. It must be noted that hydrolysis will not continue to the formation of the stannate ion, n = 6, in acidic or neutral solution. This ion exists only in crystals and in very basic solutions. When there is an OH group attached to a Sn(IV) species, there exists a strong tendency for that species to form an Sn-O-Sn bond. Thus, polymerization, the formation of large Sn-O-Sn bonded structures, ensues when hydrolysis is not repressed. The rate of formation of polymer is different for $SnCl_6^{=}$ and $SnBr_6^{=}$. When ammonium hexachlorostannate is dissolved in water, the solution becomes turbid after a short time. But when ammonium hexabromostannate is dissolved in water, the solution becomes turbid instantly, indicating the presence of colloidal Sn-O-Sn bonded structures.

The primary method of investigation in this study is spectrophotometry. Normally, halide complexes have two "sets" of absorption peaks. One set is due to electronic transitions within the central atom. These peaks are usually in the visible or near UV region of the spectrum. For Sn(IV) these peaks are not expected because it has a filled shell configuration. That is to say, it has a krypton core plus ten d electrons. The other set of absorption peaks are due to the "charge transfer" process. The term, charge transfer, refers to the photo-induced electron transfer between the halogen and the metal. These peaks are usually well within the UV region of the spectrum and also usually have intensities one hundred to one thousand times those of the other set of peaks. Orgel (10) has given examples in his review. Also he explains the well known fact that many bromide charge transfer spectra have double absorption peaks separated by 0.49 to 0.60 ev. This is presumably due to the difference in the two electronic states of the free Br atom, $^2P_{1/2}$ and $^2P_{3/2}$. Katzin (11) has reviewed the absorption spectra of many halide compounds and has noted certain similarities. Jorgensen (12) has treated theoretically, from ligand field concepts, the electronic transitions for several MX_6^{-n}, including $SnCl_6^{=}$. The type of transition should be the same for the $SnBr_6^{=}$ ion. He denotes this transition as $\pi \rightarrow \gamma_1$, which means that the electron is transferred, by interaction with a photon, from a π orbital on the halogen to the 5s orbital on the Sn(IV).

Notation.--Since spectrophotometric evidence is presented throughout this study, it is necessary to explain the notation that will be used.

Optical density or absorbancy, D, is defined as $\log I_o/I$. I_o

is the intensity of the light transmitted through a reference solution, and I is the intensity of light transmitted through the solution being examined. An equation expressing the relationship between D and the concentration c, in moles per liter, of the absorbing species is

$$D = a_m cl$$

The proportionality constants are l, the length of the light path, in cm and a_m, the molar absorbancy index of the absorbing species.

At a certain wavelength (or wavelengths) the absorbancy index has a maximum (or maxima) for the absorbing species. These wavelengths are denoted by λ_{max}, and the value of a_m at λ_{max} is denoted by a_{max}. The molar absorbancy index at a particular wavelength λ is denoted by a_m.

CHAPTER II

EXPERIMENTAL

Absorption Spectra Measurements.--Two types of measurements were made: qualitative and quantitative. The qualitative measurements were made on a Beckman Model DK recording spectrophotometer. These data concern the wavelength of the absorption maxima, λ_{max}. The λ_{max} obtained in this way has an error of about three millimicrons, 3 mμ. The quantitative measurements were made with a Beckman Model DU spectrophotometer equipped with a photomultiplier. In both cases the cells used were fused silica cells with ground glass stoppers, having a $1.000 \pm .003$ cm light path. Also silica cells having a 10.000 cm light path were used. Most of the quantitative measurements were made at 25°C, regulated to $\pm$ 0.5°C by a thermostatted water jacket. Where other temperatures were used, note is made of the fact. When a series of measurements was made at a particular Sn(IV) concentration, the slit width at a given wavelength was kept constant.

Analytical Methods.--The analytical method used for bromide was that of Kolthoff and Sandell (13). Either a weighted quantity of solid in aqueous solution or an aliquot of a solution containing bromide was adjusted to a pH of about three and titrated with tenth normal $AgNO_3$ using eosin as an absorption indicator.

The analysis for Sn(IV) was a complexometric back titration, developed by Kinnunen and Wennerstrand (14). Solids dissolved in water

or Sn(IV) solutions were acidified with concentrated HCl. A known volume of 0.0100 N EDTA (ethylenediaminetetraacetic acid, sodium salt) was added to the sample. This amount was in excess of the Sn(IV) present. The pH was adjusted to 2.0 with ammonium acetate. The resulting solution was titrated with 0.0100 N thorium(IV) nitrate solution using Xylenol Orange (0.2 per cent in water) as an indicator. This procedure is based on the complexation of Sn(IV) by EDTA, in acid, in a one-to-one ratio. The excess EDTA is titrated with the Th(IV). The end point is indicated by a yellow to deep red color change caused by the reaction of the Th(IV) with the Xylenol Orange. The Xylenol Orange was kindly donated by Dr. H. Flaschka.

Another method, outlined by Kinnunen and Merikanto (15) was used as a supplement to the foregoing method. The Sn(IV) in solution was first reduced to Sn(II), which was then titrated at 15°C by 0.050 N iodine solution with starch used as an indicator. The reduction was performed using hypophosphite (HPO_3^-) and an inert atmosphere of carbon dioxide.

Because of the small quantities involved, all titrations were made using a ten ml burette which could be read to the nearest one hundredth of a milliliter.

Chemicals.--All the water used was distilled from a commercial still.

The hydrobromic acid (HBr) used was distilled from a mixture of powdered red phosphorus and C. P. 47 per cent HBr solution. The distilled acid (constant boiling, 8.65 M) was kept in polyethylene bottles. Coloration, due to tribromide ion (Br_3^-) formation, usually appeared a week after distillation. Therefore, no HBr was used which was more than

four days old. Much effort was invested in trying to prepare and store HBr more concentrated than 8.7 M. The method used was that of saturating a constant boiling HBr solution at 0°C with HBr gas. The HBr gas was obtained from a cylinder and was passed through a train consisting of copper metal (to remove any free Br_2), anhydrous calcium sulfate, and a filter of glass wool. Unfortunately, the super-concentrated HBr solutions so obtained were unstable with respect to air oxidation at room temperature, Br_3^- forming almost immediately. This ion has a large absorption maximum near 265 mμ.

Lithium Bromide solutions were prepared from Analytical Reagent grade $LiBr \cdot H_2O$. However, acidification of the concentrated solutions developed a pink-orange color. A subsequent examination of the visible and UV spectrum revealed a large peak at 280 mμ and several smaller peaks in the visible region. This suggested that the impurity was a transition metal halide complex; iron and copper were indicated by simple qualitative tests. An anion-exchange resin (Dowex-1) in the bromide form was employed to remove the impurities. The purified concentrated LiBr solutions were colorless and the aforementioned absorption peaks were absent.

Acetonitrile as purchased usually contains some water and other impurities. The acetonitrile used in these experiments was purified by refluxing four hours with P_2O_5, distilling into anhydrous K_2CO_3, and redistilling. The fraction boiling between 81° and 82°C was collected and stored over silica gel (non-indicating).

Analytical reagent grade isopropyl ether and ethyl ether were treated with aqueous ferrous sulfate and were washed with water to

remove peroxides. They were made anhydrous by storing over sodium (metal) wire after a preliminary drying with anhydrous $CaSO_4$.

Cyclohexane and 2,2,4-trimethylpentane were purified by fractional distillation and were stored over silica gel.

All other chemicals were C. P. or A. R. grade materials.

CHAPTER III

STANNIC BROMIDE

Discussion

Physically, stannic bromide is a transparent substance that melts about 30°C and boils at 210°C. Chemically, it is a strong "Lewis acid", i.e., it has a strong affinity for electron donating groups. It readily reacts with water in the atmosphere. A tetrahydrate, $SnBr_4 \cdot 4H_2O$, has been prepared by Lorenz (16). However, stannic bromide and the tetrahydrate in aqueous solution hydrolyse rather quickly forming HBr and Sn-O-Sn structures. Pfeiffer (17) has studied this hydrolysis and Pfeiffer, Muller, and Pros (18) have concluded that the coordination number of Sn(IV) is six and that the hydrolysis proceeds in the following manner:

$$SnBr_4 \rightarrow SnBr_4(H_2O)_2 \rightarrow SnBr_3(OH)H_2O.$$

The basis for these statements is that they isolated a compound with a ratio of Br to Sn equalling three. One must note, however, that they used extractive (into ethyl ether) techniques to obtain this compound. Thus, it is possible that the extracted species was not necessarily the predominant species in the aqueous solution. A compound prepared by Rayman and Preis (19), $Sn_3O_2Br_8 \cdot 10H_2O$, supports the hydrolysis argument. The most likely structure of this compound is

$$Br_3Sn\text{-}O\text{-}\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{Sn}}\text{-}O\text{-}SnBr_3 .$$

This compound could be formed by the union of two $SnBr_3(H_2O)_2OH$ species and an $SnBr_4$. In any event the formation of the compound would not require an Sn(IV) species with more than two oxygens.

Many organic addition compounds have been made with stannic bromide. Sisler, Schelling, and Groves (20) have studied the addition compounds of $SnBr_4$ with aliphatic ethers. Diethyl ether, tetrahydrofuran, and tetrahydropyran gave products of the type $SnBr_4$.2Ether. Lander and Kraffcyzk (21) investigated the ionic reaction of stannic bromide in ethyl ether. By conductomeric titration with lithium ethoxide, they also found that two ethers were coordinated with each $SnBr_4$.

Parti and Samuel (22) measured the absorption spectra of $SnBr_4$ vapor and found two absorption maxima, one at 306.3 mμ and another at 272.8 mμ. The separation, they noted, was 3685 cm^{-1} which is near the theoretical value. Vapor density measurements made by Carnelly and O'Shea (23) show that stannic bromide is monomeric in the gaseous state. The absorption spectrum of stannic bromide in hexane was measured by Grant (24). A maximum was found about 235 mμ. The spectrum obtained also showed a shoulder at a longer wavelength.

Preparation and Purification

Several methods of preparation were attempted, however, the most satisfactory one was the direct union of the elements.

$$Sn + 2Br_2 \longrightarrow SnBr_4$$

Granular Sn metal was slowly added to liquid Br_2, which was cooled by an ice-water bath. The resulting mixture, containing excess Sn and excess Br_2, was fractionally distilled under reduced pressure. A 50 cm frac-

tionating column packed with glass helices was used. The middle one-third fraction was retained. For spectral measurements, further purification was achieved by sublimation. All stannic bromide was stored in glass stoppered containers. In preparing solutions of stannic bromide, small crystals were removed quickly from the container and dropped into a previously weighed volumetric flask. The rate of reaction of solid stannic bromide with moisture in the air is, of course, slower than that of liquid stannic bromide. The weighings were performed in an air conditioned room with the relative humidity regulated to 30 per cent.

Absorption Spectra

The measurements of the absorption spectra can be divided into two classes, those in non-aqueous solvents and those in aqueous solvents. Although the spectrum of $SnBr_4$ in each solvent was measured out to 700 mμ, no maximum was ever observed beyond 320 mμ.

Non-aqueous Solvents.--A stock solution of 5.47×10^{-4} M $SnBr_4$ in 2,2,4-trimethylpentane was prepared. This concentration is near the saturation value of this solvent. Aliquouts of the stock solution were used to prepare ten different dilutions of the original concentration. The spectrum from solvent cutoff (approximately 200 mμ) to 400 mμ was measured for four of these concentrations and no variation of λ_{max} was noted. The absorption spectra of 1.09×10^{-4} M stannic bromide is displayed in Fig. 1. A large maximum is noted at 240 mμ. The shoulder can be accounted for by a smaller peak at 272 mμ, with $a_m^{240} = 2.5a_m^{272}$. This spectrum is in agreement with that found by Grant (24), but not with the vapor spectrum found by Parti and Samuel (22). This apparent disagreement should be resolved. To investigate the possibility of

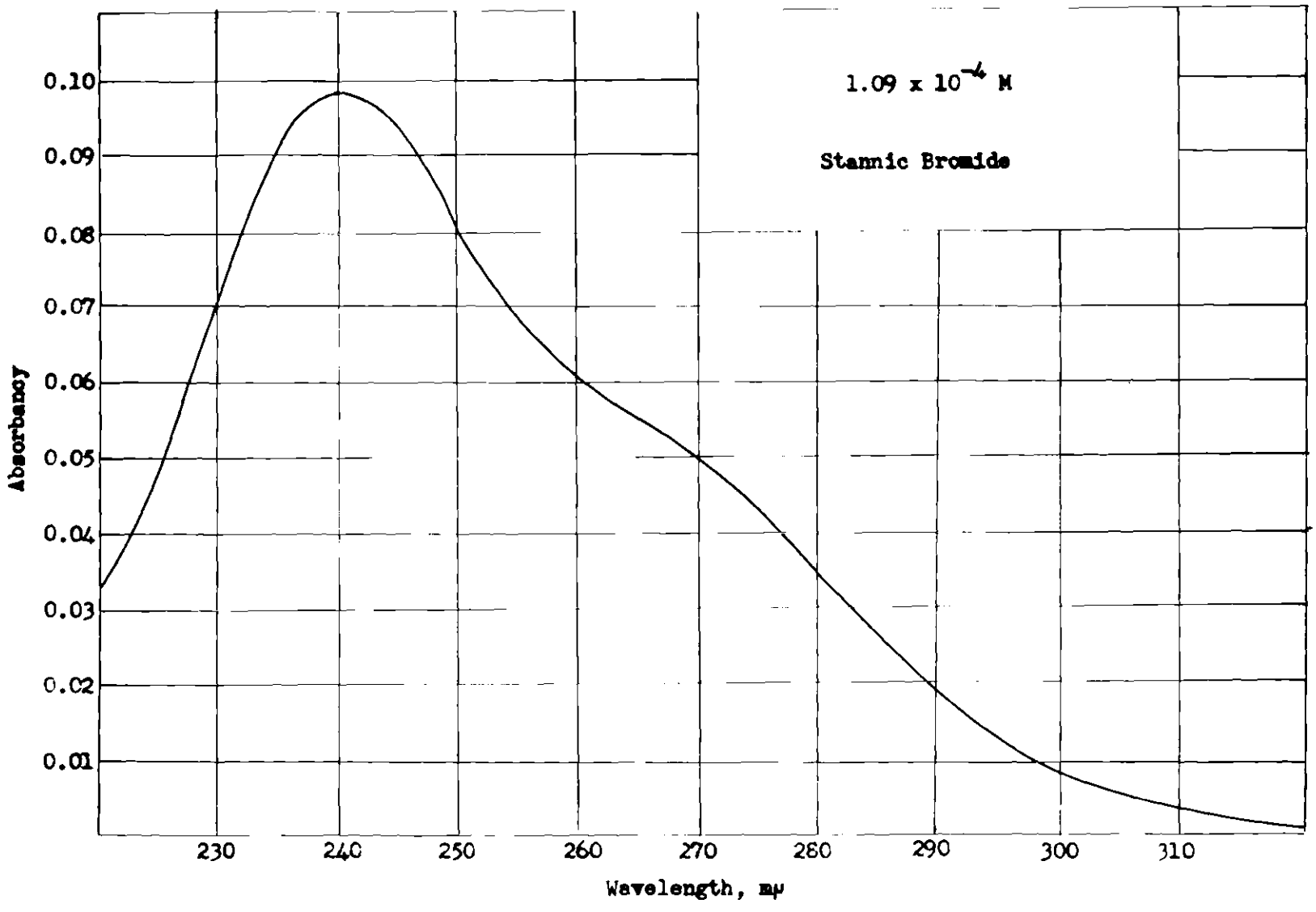

Figure 1. UV Spectrum of $SnBr_4$ in 2,2,4-trimethylpentane

equilibria between monomeric and polymeric species of $SnBr_4$ in solution. Beer's law was tested with solutions of stannic bromide in 2,2,4-trimethylpentane. Beer's law was tested by plotting the absorbancy at 240 mμ divided by the length of the cell against the concentration of stannic bromide for each of the ten dilutions. The results are shown in Fig. 2. The two points corresponding to the two smallest concentrations were measured in the 10 cm cells. An eye-fitted straight line was drawn through the points. The slope of the line is $a_m^{240} = 9200$. The least squares procedure gives the same line, which passes through the origin within experimental error. Thus, it appears that no such equilibria occur, and the spectrum displayed in Fig. 1 is assumed to be the spectrum of monomeric $SnBr_4$.

Cyclohexane and n-heptane gave spectra which were very similar; λ_{max}^{240} and λ_{max}^{272} were within 2 mμ of the 2,2,4-trimethylpentane solution absorption peaks. Also the ratio of a_m^{240} to a_m^{272} for each of the spectra was close to 2.5 (within 0.15). The a_m^{240} for stannic bromide in each of these solvents was of the order of 10,000.

The spectra of stannic bromide in ethyl ether, acetonitrile, and chloroform were also measured. All of these solvents showed what appeared to be a single peak very near the cutoff (a shoulder). It was impossible to determine if there was a second peak at yet shorter wavelengths. The values of λ_{max} were 248 mμ, 255 mμ, and 250 mμ, respectively. Their absorbancy indexes were of the order of 5,000, which is about half of a_m^{240} for $SnBr_4$ in non-polar solvents. The ether solution was observed over a seven day period, but λ_{max} did not appear to shift. On the contrary, if anything, it became more distinct.

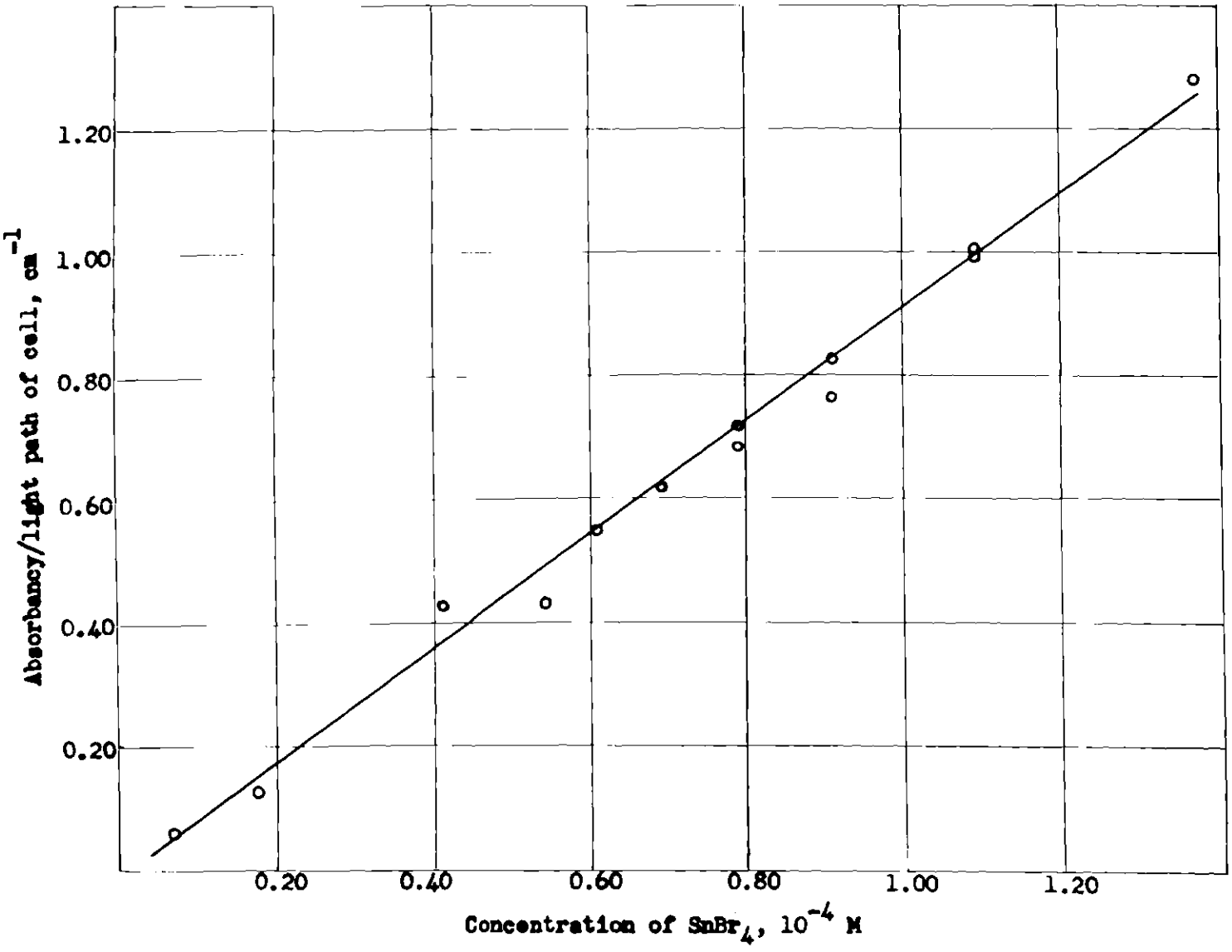

Figure 2. Test of Beer's Law in 2,2,4-trimethylpentane

It is apparent that stannic bromide in these polar solvents does not have the same spectrum as non-polar solutions. Presumably, an $SnBr_4$.nSolvent species is responsible for the spectrum.

When stannic bromide was added to tributylphosphate, a dark color formed which quickly dissipated. Subsequent examination of the solution failed to reveal any absorption maxima. Carbon tetrachloride possesses an unsuitable UV cutoff.

Aqueous Solvents.--Although concentrated sulfuric acid is considered as an aqueous solvent, it actually behaves as an inert solvent in this study. The solubility of stannic bromide in concentrated H_2SO_4 is extremely small, as it is in the hydrocarbons. The absorption spectrum shows a large maximum at 235 mμ and a shoulder at 267 mμ. The ratio of the absorbancies is three. Note should be made of the close correspondence to the hydrocarbon solutions spectra. The main difference between the two spectra is a five millimicron shift to shorter wavelengths for the sulfuric acid solution.

In water, of course, stannic bromide rapidly hydrolyzes, and a spectrum is not obtainable. Even in ethyl alcohol the hydrolysis is too rapid to obtain a spectrum. The general reaction is

$$SnBr_4 + 2H_2O \rightleftharpoons SnBr_4(H_2O)_2$$

followed by

$$SnBr_4(H_2O)_2 + nH_2O \rightleftharpoons SnBr_{(4-n)}(OH)_{(n+m)}(H_2O)_{(2-m)}^{-m} + nBr^- + (n-m)H^+$$

where m = 0, 1, or 2 and n = 0, 1, 2, 3, or 4. Accordingly, high concentrations of bromide ion should repress hydrolysis. A few crystals

of stannic bromide were dissolved in aqueous nine molar LiBr solution, and the spectrum was measured. The crystals dissolved very slowly. Even though the concentration of stannic bromide was high (approximately 10^{-2} M), only a very small peak was found at 290 mμ and a shoulder near the cutoff. The same solution was checked again after two days, and five days. The only appreciable change was that the peak and shoulder were slightly more distinct than earlier. The shoulder, about 240 mμ, seemed to be about three times as large as the 290 mμ peak. The solution was then made about 0.9 M in HBr. The spectrum of this acidified solution showed an amazing change; a huge double peak had appeared with λ_{max} at 280 mμ and 305 mμ approximately. The solution had to be diluted to less than 0.01 of its original concentration to reduce the absorbancy to the order of magnitude one.

It is fairly obvious at this point that some complexation of the stannic bromide was caused by the added HBr. Therefore, some crystals of stannic bromide were dissolved in 8.7 M HBr, which produced an amber solution. Portions of this solution were then dissolved in various media, and the spectra measured.

The results of the absorption spectra measurements of a portion of the $SnBr_4$-HBr solution dissolved in various concentrations of HBr are shown in Fig. 3. A large double peak is displayed in the concentration range of nine molar to seven molar HBr. At six molar HBr a different absorption peak is shown (λ_{max} at 270 mμ) which has a trace of the double peak in the tail. For the four and five molar cases, it is difficult to determine the maxima due to the broadness of these peaks. It is necessary to note that the concentrations of Sn(IV) in

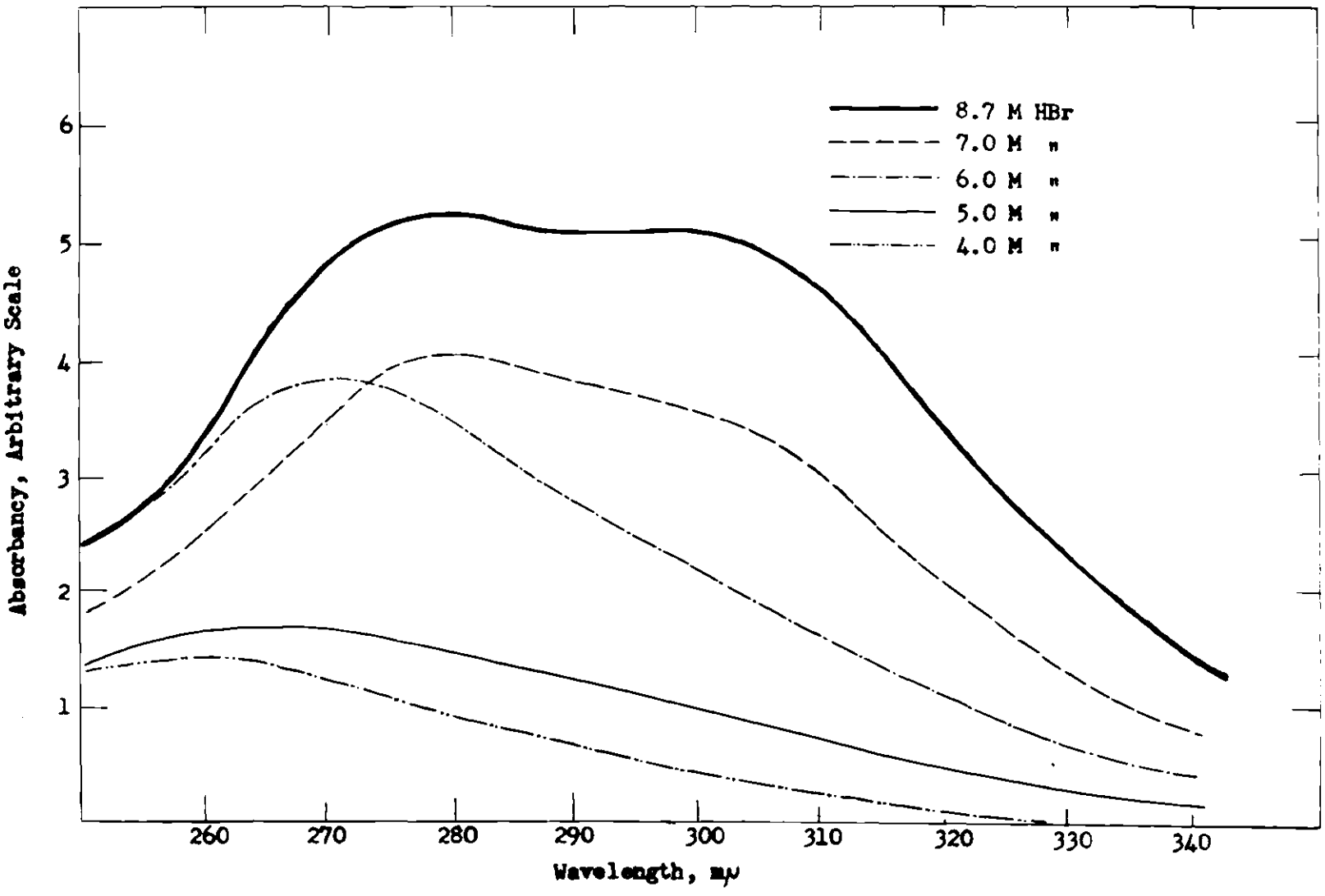

Figure 3. UV Spectra of Stannic Bromide in Various Concentrations of HBr

these solutions are not equal (but do not differ by more than 20 per cent), and therefore, quantitative arguments cannot be made. Conclusions about the behavior of these solutions will be deferred until chapter six.

When a small amount of the $SnBr_4$-HBr stock solution was dissolved in ethyl ether, the spectrum showed a single, well-defined peak at 265 mμ. It should be noted here that in Fig. 3 there is a 270 mμ peak in the six molar HBr case.

CHAPTER IV

THE HEXABROMOSTANNATES

Discussion

Hexabromostannic acid, H_2SnBr_6, and its various salts have long been known. One of the first preparations of these compounds was performed by Rayman and Preis (19), who prepared not only the eight hydrate of the acid, $H_2SnBr_6.8H_2O$, but also the six hydrates of the calcium and sodium salts, $CaSnBr_6.6H_2O$ and $Na_2SnBr_6.6H_2O$. Let it be noted that these workers claim these compounds to be colorless. Seubert (25) reports the preparation of $H_2SnBr_6.9H_2O$ and $H_2SnBr_6.7H_2O$ and the six hydrated sodium salt. He correctly identifies the colors as amber. Costeanu (26) prepared Rb_2SnBr_6 (brown), Cs_2SnBr_6 (red-violet), and $BeSnBr_6.10H_2O$ (yellow). He reports that each of these was obtained from a yellow solution. All the foregoing authors used the same procedure to obtain the salts and acid. This consists of concentrating an aqueous solution containing stannic bromide and the bromide of the cation. The concentration is achieved by slow evaporation of the solution in a dessicator containing concentrated sulfuric acid or anhydrous calcium chloride. The most recent preparations involve a slightly different procedure. De Celis and Quiros (27) dissolve the metal bromide in methyl alcohol and then add a stoichiometric quantity of stannic bromide to the solution. The alcohol is then evaporated at approximately 40°C. In this manner they prepared ten metal salts and the eight hydrate of the acid. It is well to note here that only the ammonium, potassium

rubidium, and cesium salts are non-hydrated and also that these salts are the only ones which are neither deliquescent nor efflorescent.

Many times the work of Leteur (28) is incorrectly cited for the preparation of the hexabromostannates. Leteur calls his compounds bromostannates, but they are actually the tetrabromostannates (Sn(II) bromo-salt complexes). Apparently no published data are available on the spectra of the hexabromostannates(IV). However, an analytical paper by Nielsch and Boltz (28) concerns the spectrum of stannic bromide in 48 per cent hydrobromic acid, which, of course, is equivalent to a solution of H_2SnBr_6. By the use of filters, they study the absorption at 366 mμ of various concentrations of Sn(IV) in the acid medium. They find that Beer's law is obeyed in the region from 8.0 micrograms of Sn(IV) per ml (6.74×10^{-5} M) to 1200 micrograms per ml (1.01×10^{-3} M). They also present a plot of absorbancy versus HBr concentration. The absorbancy increases steadily as the HBr concentration changes from 14 per cent to 43 per cent and then becomes almost constant for higher HBr concentrations.

Preparation

The compounds were prepared by concentration techniques which were used by the earlier workers. Three stable compounds were prepared: potassium hexabromostannate(IV), K_2SnBr_6, ammonium hexabromostannate(IV), $(NH_4)_2SnBr_6$, and n-butylammonium hexabromostannate(IV). The last of these was prepared because of anticipated use in organic solvents such as acetonitrile. The solubility of substituted ammonium salts is much better than that of salts of metal cations in acetonitrile. Also the substituted ammonium salts are "electrolytes" in acetonitrile (30).

The actual preparation of the salts was quite simple. A saturated solution of the bromide of the cation was added to a solution of stannic bromide in dilute hydrobromic acid. The resulting solution was partially concentrated by evaporation at approximately 80°C. The final product was obtained by letting the solution stand over concentrated sulfuric acid in a dessicator for several days.

The n-butylammonium bromide solution was made by drying n-butylamine over sodium hydroxide for three days, fractionally distilling the dry amine, and neutralizing the middle fraction with aqueous HBr.

All three salts were obtained as well defined yellow crystals. The potassium and ammonium salts were pseudo-cubic. Under magnification they appeared as octahedrons whose vertices had been replaced by rectangular facets. The butylammonium salt had a different crystalline form, which seemed to be tabular and hexagonal. The crystals were separated from the concentrated solutions by filtration through a sintered glass funnel. Only the butylammonium salt was washed (very rapidly with a little dry ether), for fear of decomposition. Neither were the salts dried, other than standing in air, for the same reason.

The analyses on the salts are as follows:

Compound	Analysis			Calculated	
	Sn %	Br %	Br/Sn (mole)	Sn %	Br %
K_2SnBr_6	17.5	71.5	6.07	17.5	71.0
$(NH_4)_2SnBr_6$	18.9	77.3	6.07	18.7	75.7
$(BuNH_3)_2SnBr_6$	15.5	62.5	5.98	15.9	64.2

The analysis of the butylammonium salt indicates a one-hydrate formula.

A preparation of the tetraethylammonium salt was attempted, but the compound obtained did not have the correct Br/Sn mole ratio.

All the salts were solvolyzed in water and alcohol to give colloidal decomposition products. In anhydrous ethyl ether the butylammonium salt was very sparingly soluble. Also in ether, the potassium and ammonium salts were decomposed into a soluble portion and a white crystalline insoluble residue. Approximately one gram of the ammonium salt was added to ten ml of ether. After the mixture had stood for one month, the liquid was yellow, and the solid was white. The white residue was triturated with small portions of fresh ether. Semi-quantitative tests showed that the material was mostly ammonium bromide containing traces of Sn. The butylammonium salt was quite soluble in acetonitrile, but the ammonium and potassium salts tended to leave a white residue. None of the salts were soluble in dry isopropyl ether. The spectrum of a mixture of 0.00219 g of the butylammonium salt in 25 ml of anhydrous isopropyl ether revealed, after two days, only a very small general absorption. The salt had been dried for several days in a dessicator.

These experiments indicate that the solvents which completely dissolve salt must necessarily be able to dissolve the simple bromide of the cation. Solvents in which the simple cation bromides are insoluble will simply "extract" the soluble species. The following equation formalizes the process:

$$M_2SnBr_6(\text{solid}) + nRZ \rightleftharpoons nMBr(\text{solid}) + M_{(2-n)}SnBr_{(6-n)}\cdot nRZ$$

where RZ is a polar solvent.

Absorption Spectra

Non-aqueous Solvents.--Although the solubility of the salts in ethyl ether was extremely limited, spectra were obtained because of the large absorbancy indexes of the absorbing species. In dry ethyl ether the potassium and ammonium salts gave rise to a single poorly-developed peak at 245 mμ to 250 mμ. The exact position of the peak could not be determined because of the cutoff of the solvent. This peak seems to correspond to the peak found for stannic bromide in ether, which was attributed to an $SnBr_4$.nSolvent species.

In acetonitrile the behavior was somewhat different. Qualitative measurement of the potassium salt spectrum in acetonitrile revealed a single large peak at 260 mμ. Quantitative spectral measurements of the potassium and butylammonium salts are displayed in Fig. 4. On the same figure are shown absorption spectra for the same salts in acetonitrile, to which small quantities of tetraethylammonium bromide had been added. Although the spectra are not exactly the same, the similarities are obvious. When only the hexabromostannates are added to the acetonitrile, there is a large peak in the 265 mμ to 270 mμ region. This peak has a long tail on the long wavelength side. With added bromide (tetraethylammonium salt) this peak disappears entirely and two new peaks of the same height appear at 290 mμ and 315 mμ. These peaks are very similar to those found for stannic bromide in HBr. It can be assumed that the double peaked species has a larger number of bromine atoms than the species with a peak at 265 mμ.

Aqueous Solvents.--As in the case of stannic bromide, the hexabromostannates hydrolyze almost immediately in pure water. Some bromide is

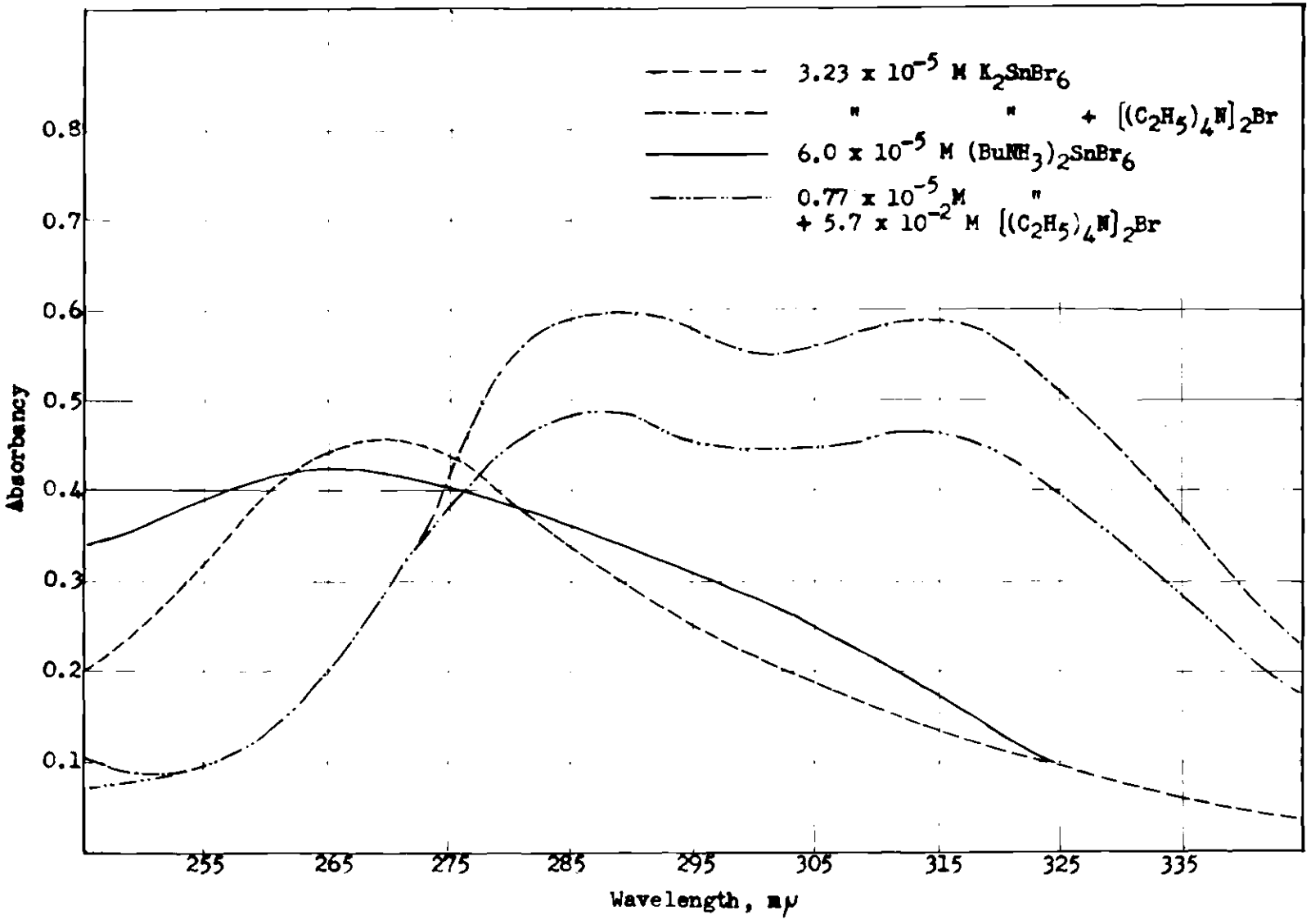

Figure 4. UV Spectra of Hexabromostannates in Acetonitrile

needed to keep the material in solution.

A solution of approximately 2×10^{-4} M ammonium hexabromostannate dissolved in 8.7 M HBr showed two equal sized peaks about 280 mμ and 308 mμ. Both the butylammonium salt and the potassium salt were checked carefully in 8.7 M HBr. The spectrum of each salt displayed a maximum at 281 mμ and a slightly smaller peak at 305 mμ. The spectral curves of the two salts were almost exactly superimposable. The potassium salt had an absorbancy index of 9500 at 281 mμ, while the butylammonium salt had one of 9000. This experiment shows that the cation of the salt does not appreciably affect the spectrum of the hexabromostannate ion in this medium. Thus, for consistency, the rest of the absorption spectra measurements were made using only the potassium salt.

Lithium bromide solutions containing HBr were used as solvents for the potassium salt. In Fig. 5 data is presented for two different measurements at different bromide and acid concentrations. Two equal sized peaks are shown which are again at 281 mμ and 305 mμ. For each solution the absorbancy index is about 9400. This experiment shows that in this bromide concentration range the hydrogen ion concentration had very little affect on the spectrum.

The next experiment shows the effect of changing bromide concentration while keeping the hydrogen ion concentration constant at 1.67 M. A stock solution of 3.29×10^{-4} M potassium hexabromostannate in an aqueous solution of HBr and LiBr was prepared. Analysis showed the solution to be 11.9 M in bromide and 1.67 M in hydrogen ion. Another solution not containing Sn but containing the same concentrations of hydrogen ion and bromide was prepared. A third solution of 1.67 M HBr

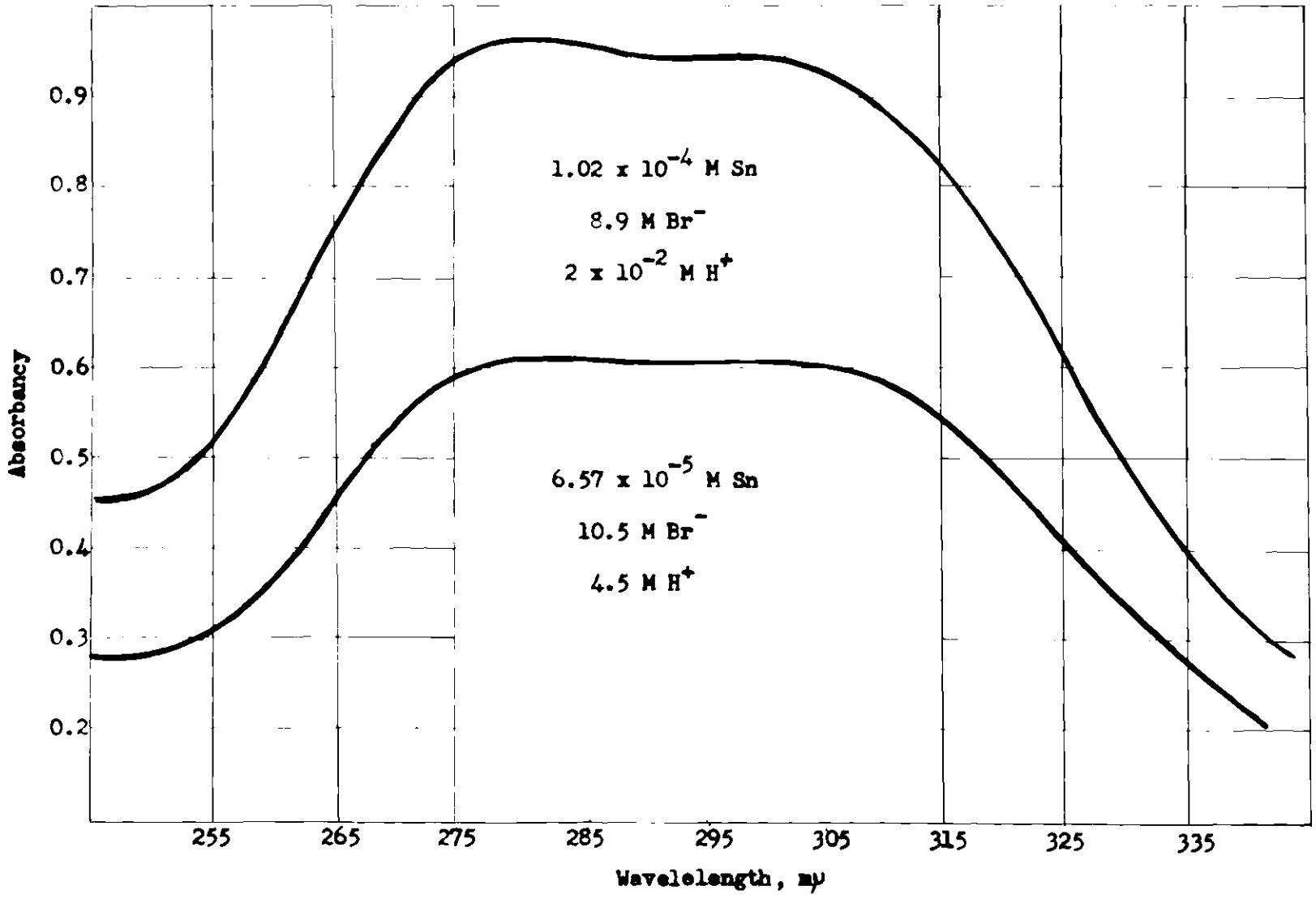

Figure 5. UV Spectra of K_2SnBr_6 in Aqueous LiBr-HBr Solutions, I.

in water was also prepared. The samples were made by using 1.0 ml of the stock solution and 4.0 ml of combined solutions two and three. A reference solution was prepared in the same manner except that the 1.0 ml of stock Sn solution was replaced by 1.0 ml of the second solution. The results of the spectral measurements are shown in Fig. 6. The characteristic twin peaks at 281 mμ and 305 mμ decrease as the bromide concentration decreases. However, the 281 mμ peak does not decrease regularly as does the 305 mμ peak. The reason for this behavior is indicated by the appearance, at 5.8 M Br^-, of a broad peak about 255 mμ. Apparently this peak increases slowly as the double peak decreases. Thus, the 281 mμ peak appears to decrease at a different rate than the 305 mμ peak. We conclude then that the double peak must be characteristic of the hexabromostannate ion. As the bromide concentration decreases, the equilibrium shifts to the hydrolyzed species. The 255 mμ peak represents one of these hydrolyzed species.

A corresponding set of experiments was performed in which the hydrogen ion concentration was varied, while the bromide cencentration was kept constant. Again three solutions were prepared. Two solutions were LiBr, pH of 1.8, one of which contained 3.78×10^{-4} M potassium hexabromostannate. The third solution contained only HBr. All the solutions were 7.05 M in Br^-. The samples were made by using 1.0 ml of stock Sn solution and diluting with 6.0 ml of a combination of the other two solutions. The reference solutions were comparable to the samples. The absorption spectra are shown in Fig. 7. The peaks for the 1.0 M and 7.0 M hydrogen ion cases are very similar and show the same shape as that in the 7.8 M Br^- case in Fig. 5. When the hydrogen

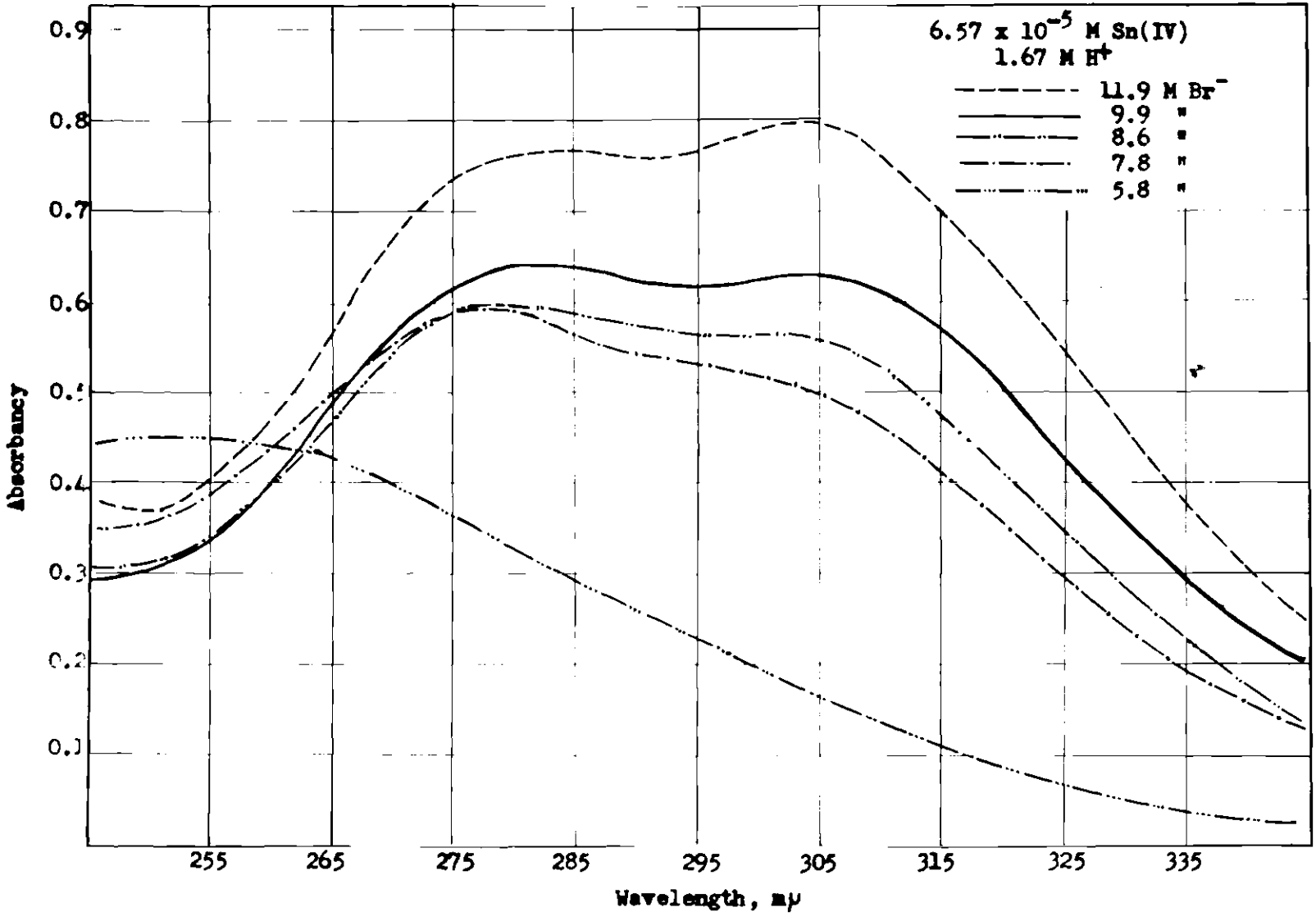

Figure 6. UV Spectra of K_2SnBr_6 in Aqueous LiBr-HBr Solutions, II.

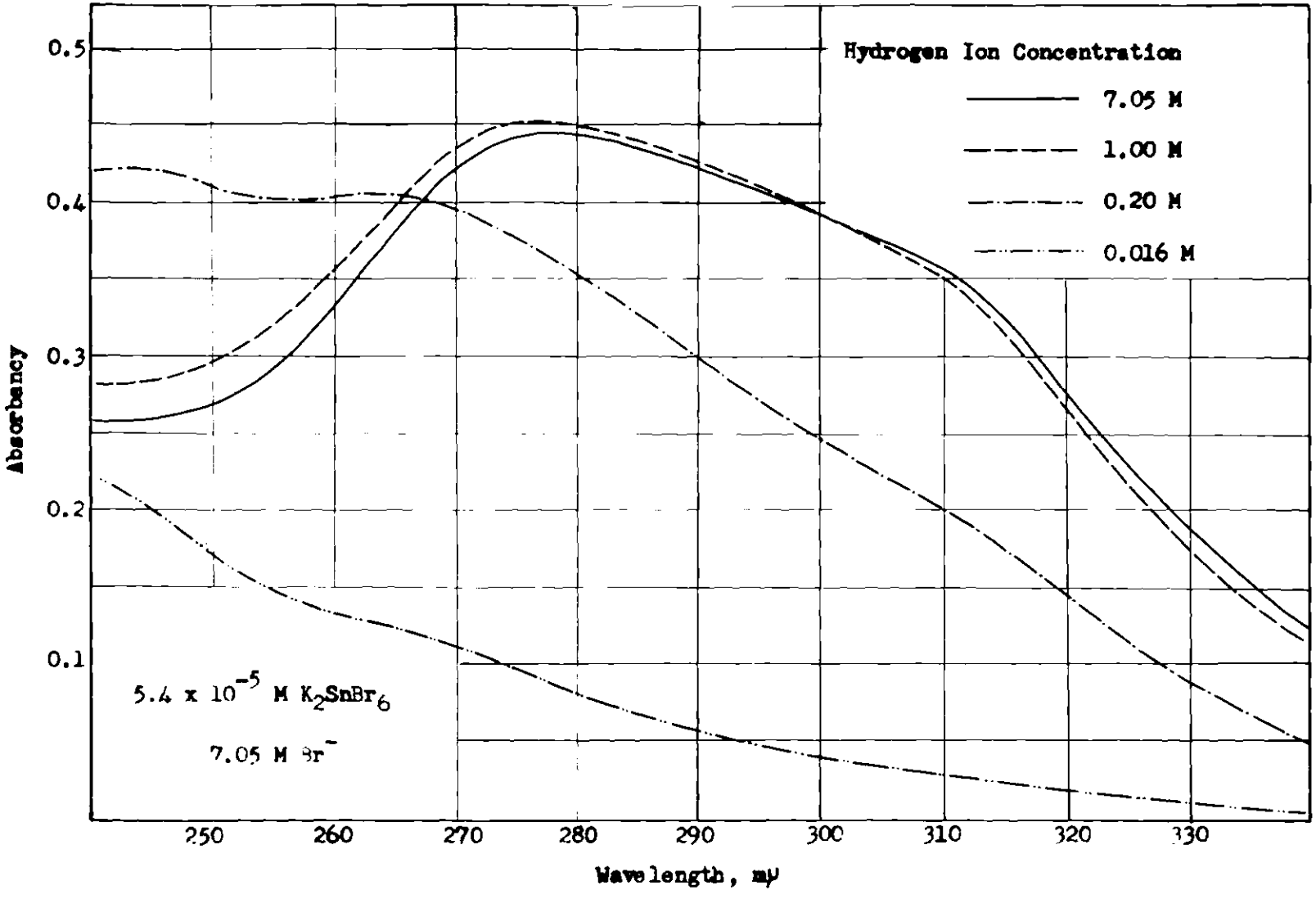

Figure 7. UV Spectra of K_2SnBr_6 in Aqueous LiBr-HBr Solutions, III.

ion concentration becomes smaller than one molar, then absorption maxima appear at longer wavelengths which indicates that the hexabromostannate is hydrolyzed to species with fewer than six bromines. The absorption spectra for the two lower concentrations seem to show two maxima about 265 mμ and 245 mμ. We have shown earlier that the 245 mμ peak is probably a four brominated species. Since the 265 mμ peak decreases with decreasing hydrogen concentration, it is a species intermediate between the hexabromostannate and the 245 mμ species.

CHAPTER V

MISCELLANEOUS DATA

Solvent Extraction.--The technique of solvent extraction is of interest because of its application to Sn(IV) halo-complex systems. Sn(IV) can be extracted into diethyl ether from aqueous solutions of HCl and of HBr. Since Sn(IV) is complexed in these solutions, extraction data should provide information about important factors in such ion-association extraction systems. Halo-complexes which show good extractability into ether are characterized by a single negative charge. Some of these complexes are $FeCl_4^-$, $AuCl_4^-$, $TlCl_4^-$, $SbCl_6^-$, $GaCl_4^-$, and $InBr_4^-$. Kraus, Nelson, and Smith (31) have discussed this property in connection with the absorption of such complexes on anion exchange resins. A charge of minus one seems to be a necessary, but not sufficient, condition for ether extraction. In view of this it is improbable that Sn(IV) is extracted as $SnCl_6^=$ and $SnBr_6^=$, but it is not impossible.

In favorable systems where the metal appears only as the extractable ion throughout the acid concentration range, the extent of extraction will change with acid concentration because of the changing nature of the solvent phases. For most organic solvents this produces a maximum extraction at an acidity characteristic of the solvent and acid, but independent of the particular metal complex extracted (32, 33). Maximum extraction of Fe(III), Ga(III), and Tl(III) into ethyl ether from HCl occurs at 7.0 M HCl; for extraction from HBr the maximum occurs at 4.5 M

HBr for Ga(III), In(III), Tl(III), Tl(I), and Fe(III). Conversely, Sn(IV) possesses a maximum extractability (per cent of total metal ion extracted) of 20 per cent at 4.2 M HCl (34), and of 86 per cent at 4.2 M HBr (35). This inconsistancy suggests that the equilibria between Sn(IV) species in the aqueous phase are responsible. A complex species which has a single negative charge, and is a likely hydrolysis product is $Sn(H_2O)X_5^-$. This species and possibly $Sn(H_2O)_2X_4$ should be the major ether extractable species, not $SnX_6^=$.

In the following experiments isopropyl ether was used because it is less volatile than ethyl ether, yet possesses transparency in the near UV region of the spectrum. In all of the experiments the ether was first saturated with water. Also in each of the experiments equal volumes of ether and HBr solution were used. Room temperature (about 25°C) prevailed.

Solutions of potassium hexabromostannate which were 8.7 M, 6.0 M, and 3.8 M in HBr were extracted with ether. Blank solutions of HBr of the same molarity were also extracted. The absorption spectra of portions of the ether phase were then measured using the ether phase of the blank experiments as reference solutions. The results of these measurements are shown in Fig. 8. Although the concentration of Sn(IV) is not the same for each spectrum, the general features of the spectra are apparent. For the 6.0 M and 3.8 M HBr experiments there appears to be a single broad peak close to the cutoff at 260 mμ. In the 8.7 M HBr experiments a shoulder appears in the 300 mμ region. This clearly indicates that the 260 mμ species is the major extractable species, but that extraction from concentrated HBr solutions yields some different minor species

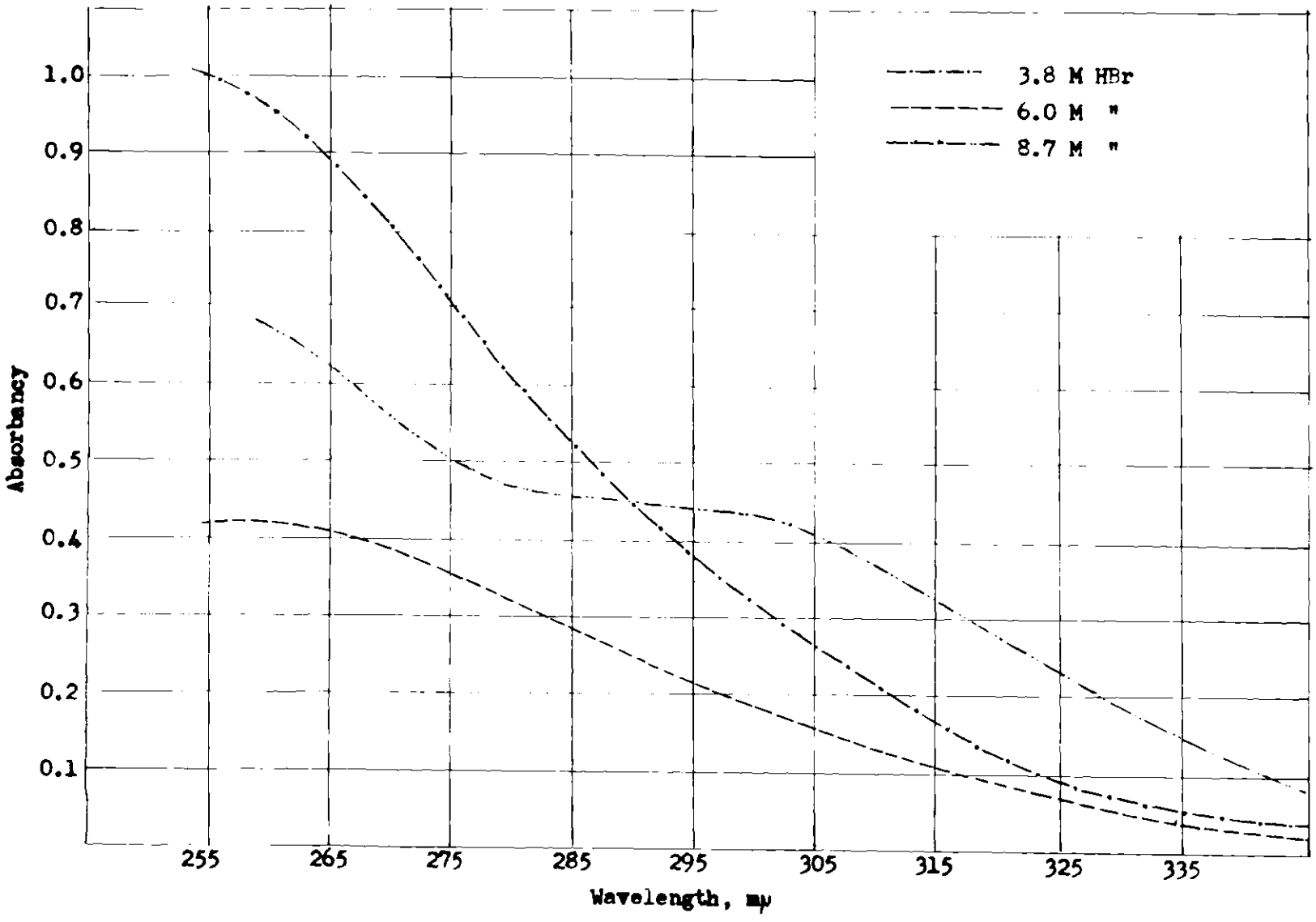

Figure 8. UV Spectra of Sn(IV) Extracted from HBr by Isopropyl Ether

with λ_{max} near 300 mμ. These spectra can be interpreted to suggest that the 300 mμ peak is caused by minor amounts of the hexabromostannate ion, and that the major extracted species, with a maximum near 260 mμ, is a five bromo-Sn(IV) complex.

Assuming that enough of the Sn(IV)-Br species can be obtained in the ether phase, it should be possible to analyze for the Br/Sn mole ratio. This experiment was tried. Hexabromostannate salts dissolved in three different concentrations of HBr were extracted with ether. Blanks were also extracted at the same time under the same conditions. Aliquots from the organic phase of the blank and sample were mixed with equal volumes of one molar NaOH solution. The mixture was then slowly evaporated to transfer the Sn and Br to the alkaline solution. The alkaline solution was then analyzed for Sn and/or Br by methods previously mentioned. Only the attempts of analysis for the 3.8 M HBr case met with any success, and this with only partial success. The reason for failure was that to obtain the Br/Sn ratio for the extracted species, the concentration of Br in the blank was subtracted from the Br concentration in the sample. In the 8.7 and 6.0 M HBr cases the bromide concentration in the blank was very near the bromide concentration is the sample. Thus, the difference of the two concentrations was inaccurate.

Three values for the Br/Sn ratio of the extracted species were obtained. The Sn concentration in each case was of the order 10^{-4}; the Br^-, 10^{-3} M. The values were 5.17, 4.78, and 5.62. It is clear that the species extracted into isopropyl ether from 3.8 M HBr has an average Br/Sn mole ratio near five.

Solid State Spectrum.--The solid state spectra of metal ions has become of interest in the last few years. And, surprisingly, the solid state spectra often resembles very closely the spectra of the same metal ion in solution. Borstrub and Jorgensen (36) examined the complexes of Ni(II) in solution and in solid state, and found striking similarities between the two. Glassner and Reisfeld (37) examined the UV and visible spectra of several metal ions in pressed alkali halide disks. They found that the absorption peaks in the solid state had very nearly the same wavelengths as the same metal ion in concentrated halide solutions.

Since the alkali halides are transparent over most of the spectrum, and since the hexabromostannate ion exists in the solid state, it was natural to apply the KBr pressed disk technique to the problem. Dry, pure KBr was powdered in an agate mortar. Some of the material was saved to make a reference disk. Dry K_2SnBr_6 was ground with the remaining KBr. Over fifty one-half inch diameter disks were made before a pair, sample and reference, which had the same weight and clarity, were obtained. The disks were formed in a hydraulic press giving a pressure of 25,000 psig. Special cylindrical blackened brass holders were made which fit the DU spectrophotometer in the usual place for the 10 cm quartz cells. The spectrum obtained is shown in Fig. 9. The concentration of potassium hexabromostannate was 0.01 per cent by weight, but the light path was very short, less than 0.40 mm. Two peaks are evident, one at 335 mμ and the other at approximately 290 mμ. Clearly, this could only be the spectrum of the $SnBr_6^=$ ion since neither potassium ions nor bromide ions absorb in this region of the spectrum.

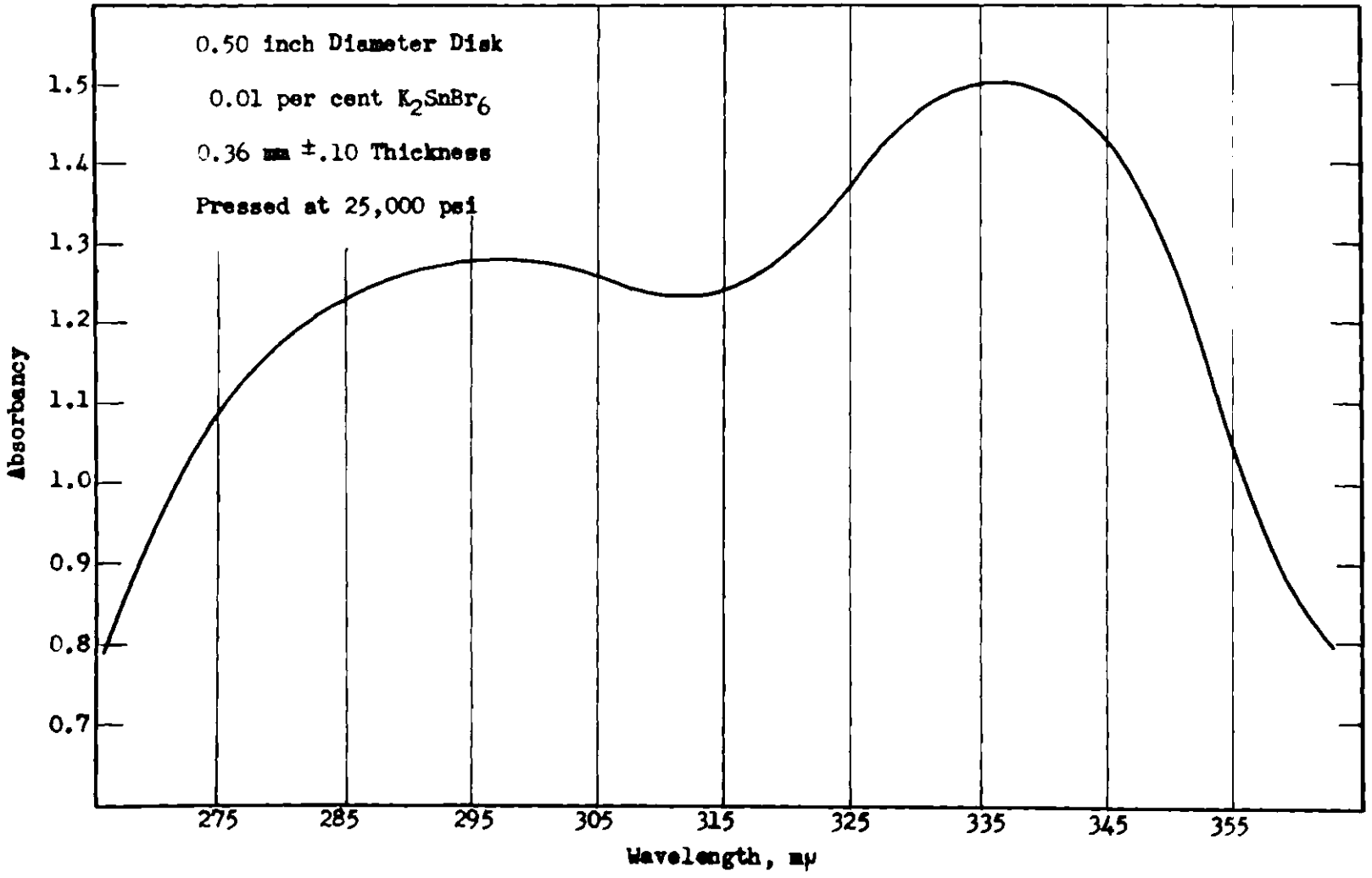

Figure 9. UV Spectrum of K_2SnBr_6 in Solid KBr (pressed disk)

The maxima do not coincide with those found in concentrated bromide solutions, but this anomaly does not invalidate either spectrum. In any case, the solid spectrum shows a double maximum as does the solution spectrum.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The absorption spectrum of stannic bromide was determined conclusively in the non-polar, non-aqueous solvents. The maximum at 240 mμ and shoulder at 270 mμ agree with the spectrum found by Grant (24). Although neither of these spectra agrees with that found in the vapor state (maxima at 273 mμ and 306 mμ) by Parti and Samuel (22), the spectra are apparently correct for the liquid state. The Beer's law test shows that no polynuclear species are present in the solvents.

In polar non-aqueous solvents a broad peak near 250 mμ was noted. It is concluded that this peak is the absorption maximum of $SnBr_4$ coordinated with two solvent molecules. The fact that many stable compounds are formed by the addition of two polar molecules to $SnBr_4$ supports this idea. Further evidence for the assignment of the 250 mμ peak to an $SnBr_4.2$Solvent species is furnished by the spectra of acetonitrile and ethyl ether which have "extracted" stannic bromide from the solid hexabromostannates. Also the addition of two molecules would just complete the coordination number of six for Sn(IV). The actual λ_{max} is probably determined by the strength of the coordinating groups as electron donors. Stannic bromide in acetonitrile, for instance, gives a peak near 255 mμ while in ethyl ether the peak is at 245 mμ. This type of behavior is also displayed in similar systems. Examples of these are ICl (38) which gives a maximum of 359 mμ in

acetonitrile and 344 mμ in methanol, but gives a maximum of 460 mμ in non-polar solvents. Also the spectrum of ICN has been measured in ether, acetonitrile, ethanol and non-polar solvents (39).

The spectrum of stannic bromide in concentrated sulfuric acid is a special case. It is clear from the spectrum obtained that molecular $SnBr_4$ exists in the solution. The extremely small solubility of stannic bromide in concentrated sulfuric acid is analogous to that in the hydrocarbon solvents.

Because of hydrolysis, the question of the type of species in aqueous solution is much more difficult to answer. Therefore, for the moment, disregard the species intermediate between $SnBr_4$ and $SnBr_6^=$. Instead, consider the spectrum of the hexabromostannate ion. It is apparent that high concentrations of HBr should ensure the existence of the hexabromostannate ion in solution. The absorption spectra of stannic bromide and each of the hexabromostannate salts in 8.7 M HBr showed two maxima; at 280 mμ and 305 mμ. Even increasing the bromide concentration to 11.9 M (with LiBr), with the hydrogen ion concentration at 1.67 M, failed to change the positions of the absorption maxima. In acetonitrile the double peak, although shifted to 285 mμ - 310 mμ, was prominent when excess bromide ion was present. The separation of the maxima in each case is near the value predicted for bromides. Thus, the conclusion is that the absorption spectrum of the hexabromostannate ion in solution is a double maximum near 280 mμ and 305 mμ.

Although the spectrum of the hexabromostannate ion in the solid state (KBr) does not have maxima at 280 mμ and 305 mμ, it does show a double maximum which has a separation comparable to that found in solu-

tions of the hexabromostannate ion. The shift of the maxima to longer wavelengths in KBr is consistent with the color of the alkali hexabromostannates. The potassium salt is yellow, indicating absorption in the violet region of the spectrum. But the rubidium salt is brown, and the cesium salt is red-violet. Both colors indicate absorption in the visible region of the spectrum. It is evident that the different electrostatic fields presented to the hexabromostannate ion by the various alkali metal ions causes the absorption maxima to appear at different wavelengths. It is suggested that the reflection spectrum of the several alkali hexabromostannates be measured or, alternatively, that the absorption spectrum of the hexabromostannate ion in pressed disks of various alkali bromides be measured. These experiments would determine the direction and magnitude of the spectral shift.

Now the absorption spectra of Sn(IV) in solutions of various bromide concentrations may be analyzed. In Fig. 6 it can be seen that the size of the hexabromostannate peaks decreases with decreasing bromide concentration. In the lowest concentration of bromide almost all of the Sn(IV) is in a species having an absorption maximum at 250 mμ. A 250 mμ maximum was earlier shown to be characteristic of an $SnBr_4.2$-Solvent species. The conclusion is that the hexabromostannate is hydrolyzed to a tetrabromostannate(IV) species. This would suggest $SnBr_4(H_2O)_2$ as the species. Because of the electrophilic nature of $SnBr_4$, the species $SnBr_4(H_2O)_2$ should be acidic leading to the presence of $SnBr_4(H_2O)(OH)^-$ and $SnBr_4(OH)_2^=$. The relative amounts of these species will depend on the concentration of hydrogen ion in the solution. It is possible that these species are sufficiently acidic such that

$SnBr_4(OH)_2^=$ is the predominent form present when the hydrogen ion concentration is 1.67 M. It is recommended that absorption spectra measurements be made on an Sn(IV) system in which the hydrogen ion concentration is higher than that of the bromide concentration. This would necessitate introducing anions other than Br^- into the system.

Evidence for the species containing five bromides is inconclusive. One would expect this species to have an absorption maximum between those of the four and six bromo species. This region is 260 mμ to 270 mμ. Indeed two experiments did show a definite peak in this region. Stannic bromide in HBr when dissolved in ethyl ether displayed a peak at 265 mμ. Butylammonium and potassium hexabromostannate dissolved in acetonitrile gave rise to a peak at 270 mμ. There are other indications and suggestions of a peak near 265 mμ. In the experiments with $SnBr_4$ in HBr, Fig. 3, there is an indication of a peak at 270 mμ in the six molar HBr case. However, this could be a combination of other peaks. Similarly, in the experiments of varying acidity with constant bromide concentration (7.05 M), Fig. 7, there are definite suggestions of a peak in the 270 mμ region at the two lowest acid concentrations. The conclusion is that if the $SnBr_5$.Solvent species exists, then it must have a small absorbancy index or it must not exist in large concentrations under ordinary conditions. One factor which dictates against the stability of the $SnBr_5$.Solvent species is the asymmetry as compared to the $SnBr_6^=$ and the $SnBr_4$.2Solvent species.

The course of the hydrolysis of the hexabromostannate ion can now be constructed.

$$SnBr_6^{=} + H_2O \rightleftharpoons SnBr_5OH^{=} + H^+ + Br^-$$

$$SnBr_5OH^{=} + H_2O \rightleftharpoons SnBr_4(OH)_2^{=} + H^+ + Br^-$$

Nothing can be concluded about further hydrolysis steps.

The importance of the hydrogen ion in complexing reactions must not be overlooked. Stannic bromide, when dissolved in neutral nine molar LiBr solution showed an extremely small hexabromostannate peak even after a week, but no 265 mμ peak. Thus, the reaction,

$$SnBr_4(OH)_2^{=} + Br^- + H^+ \rightleftharpoons SnBr_5OH^{=} + H_2O$$

and subsequent reactions were driven far to the left even though the bromide concentration was high. In 7.05 M Br^- solutions, changes in the hydrogen ion concentration have a negligible effect on the spectrum (Fig. 7) when the hydrogen ion concentration is above 1.0 M, but have a great effect when the hydrogen ion concentration is small. For a particular bromide concentration there is a hydrogen ion concentration level, above which further increases do not appreciably affect the spectrum. Under these conditions the relative amounts of the hexabromo and pentabromo species remain unchanged. The lack of a hydrogen ion dependence in 1.0 to 7.0 M HBr suggests that $Sn(H_2O)Br_5^-$, rather than $Sn(OH)Br_5^{=}$, is the pentabromo species in 7.05 M Br^- solutions.

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